



(19)

Europäisches Patentamt
European Patent Office
Office ur p'end s brevets



(11)

EP 0 709 507 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
01.05.1996 Bulletin 1996/18

(51) Int. Cl.⁶: D04H 1/64

(21) Application number: 94309133.0

(22) Date of filing: 07.12.1994

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE

• Kapadia, Surendra Nanalal
West Croydon Surrey CR0 3BU (GB)

(71) Applicant: VINAMUL LTD.
Carshalton, Surrey SM5 2JU (GB)

(74) Representative: Wiesenhaan, Herman, Drs.
Looermark 1
NL-7437 SH Bathmen (NL)

(72) Inventors:
• McLennan, Alistair John
Hackbridge Surrey SM6 7HL (GB)

(54) Sanitiser in polymer and its use in non-wovens

(57) The invention provides a sanitiser incorporated in a polymeric composition which polymeric composition comprises vinylester and alkyl(metha)acrylate and/or ethylene and at least one post polymerisation crosslinkable monomer. Preferably the polymeric composition comprises vinylacetate and alkylacrylate (e.g. butylacrylate or 2-ethylhexylacrylate) and as crosslinkable monomer N-methylolacrylamide and/or an alkylester of N-methylolacrylamide. It is preferred that the weight ratio of vinylacetate : alkylacrylate: crosslinkable monomer is from 30 - 80 : 20 - 70 : 0.5 - 10. Preferably the sanitiser comprises a halogenated phenol derivative, especially 2,2'-dihydroxy-5,5'-dichloro-diphenylmethane (Panacide).

EP 0 709 507 A1

Description

This invention relates to certain polymeric compositions intended for use as a binding composition for fibrous materials such as viscose and polyester so as to obtain non-woven materials and to the non-woven materials obtained.

Certain non-woven materials such as wiping cloths ("wipes"), packaging materials, non-woven bandages etc. function often as short lived disposable articles because after some use they are prone to rapid biodeterioration. Moreover prolonged use of e.g. wiping cloths may lead to bad sanitary conditions e.g. due to undesired spread of bacteria and moulds. That is why such articles are usually discarded after having been used only once. Washing may help to extend the lifespan of these articles somewhat but is often found too cumbersome.

The present invention aims at providing certain non-woven articles such as wiping cloths etc. having a longer resistance to biodeterioration and a longer lifespan than is normally available, and the usage of such non-woven articles may help to improve sanitary conditions in hospitals, laboratories, catering establishments and households in general. Consequently "wipes" for industrial and domestic use are provided.

The present invention also provides certain polymeric compositions suitable as binding compositions for the non-woven articles according to the present invention.

European Patent Specification (EP-A-) 0 201 214 (Nippon Paint Co., Ltd) discloses polymeric microparticles containing pesticidal agents such as e.g. biocides against various organisms. These microparticles can be formulated in aqueous and non-aqueous formulations and serve for protecting various industrial products such as coating compositions, electric wire coverings, plastic products and the like, from being attacked by noxious animals and plants.

In a first embodiment the present invention provides a sanitiser incorporated in a polymeric composition comprising vinylester and alkyl(metha)acrylate and/or ethylene and at least one post-polymerisation crosslinkable monomer.

In another embodiment the invention provides a non-woven material comprising a polymeric composition with incorporated sanitiser.

Under a sanitiser is here to be understood a composition having a number of valuable properties such as microbicidal and fungicidal activity, a good human skin compatibility, stability and should be non-volatile and soluble in oil. Preferably a sanitiser is also of low toxicity to humans and has no adverse effect on the degradation activity in sewage plants. Suitable sanitisers according to this invention are certain halogenated phenol derivatives. Dicyclic chlorinated phenol derivatives are generally preferred. Particularly preferred is 2,2'-dihydroxy-5,5'-dichloro-diphenylmethane (Panacide tradename Coalite Chemicals U.K.). This latter compound has an especially favourable combination of properties. Other useful sanitisers are e.g. 2,4,4'-trichloro-2-hydroxydiphenylether (tradename Triclosan), available from Ciba Dyes and Chemicals; 4-chloro-3,5-xylenol (PCM), available from Nipa Laboratories as Nipacide PX (Nipacide is a tradename); 5-chloro-2-hydroxy-diphenylmethane (Chlorophene), available from Nipa Laboratories as Nipacide BCP; 2,4-dichloro-3,5-dimethylphenol (DCMX), available from Nipa Laboratories as Nipacide DX; 4-chloro-3-methylphenol (PCMC), available from Nipa Laboratories as Nipacide PC, orthophenyl (OPP), and chlorinated derivatives as e.g. available from Coalite Chemicals under the tradename Cotane. The invention covers the use of any of the above sanitisers. Panacide, Triclosan and Chlorophene are preferred sanitisers and Panacide is particularly preferred. Mixtures of more than one sanitiser can also be used often with favourable results. Preferably sanitiser(s) is (are) present at a level of about 0.1 to 5% (w.w.) calculated on the amount of monomeric material, but the exact level may depend somewhat on the nature of the compound(s) used.

Non-woven fibrous material comprises a consolidated mass of fibres which may be laid down by mechanical, chemical, pneumatic, electrical or vacuum means and deposited in a desired shape, for example as webs, mats or sheets, or in a three dimensional form. The fibres may be natural or synthetic or a combination. In general the fibres to be used will be selected to suit the desired end use of the non-woven product. The fibres may be derived from wood, i.e. cellulose, or may be viscose, polyester, cotton, rayon, wool etc. The fibres may be deposited in a random manner or may be deposited or aligned along particular axes. The non-woven product may contain layers of fibres oriented in a cross-layered manner to provide a uniform strength across the products.

The good quality non-woven products according to the present invention comprise a binding composition to ensure that the product maintains its physical integrity. The binding composition is introduced during or after formation of the non-woven product. Part of the binding composition will coat the fibres, but another part will be concentrated at the positions where the fibres touch. Subsequent treatment, usually by the application of heat, dries and/or cures the binding composition and gives structural integrity to the product. The non-woven product may be impregnated with the binding composition by dipping or immersing in the composition to provide sufficient pick-up. There is no restriction on the means of application of the binding composition and this can also be e.g. soaking, spraying, rolling, brushing or applying a solid binding composition in the form of a powder, particles or fibres. The non-woven product comprising the binding composition in the form of a web can then be passed between a pair of optionally heated pressure rollers to ensure the impregnation is uniform and so as to control the amount of binding composition applied.

The polymeric binding composition used according to the present invention is particularly a copolymer emulsion obtained by polymerizing unsaturated monomers in an emulsion system and more in particular a polymeric composition substantially prepared from vinyl ester and alkyl(metha)acrylate and/or ethylene and at least one post-polymerisation

crosslinkable monomer. Such copolymer emulsions can be prepared by means of processes which can be performed at ambient temperature and at atmospheric or superatmospheric pressure, e.g. up to 12,000 kPa. Suitable post-polymerisation crosslinkable monomers comprise e.g. N-methylolacrylamide and/or an alkylester of N-methylolacrylamide e.g. N-(n-butoxymethyl)acrylamide. N-methylolacrylamide and/or an alkylester of N-methylolacrylamide are particularly preferred. The presence of a post-polymerisation crosslinkable monomer improves the strength of the copolymer solid and thereby provides structural integrity to the non-woven product. The amount of post-polymerisation monomer is usually in the range of 0.5 to 10% by weight of the total monomer content.

Preferably not more than 90% by weight, more preferably between 40 and 80% by weight of the monomer content is vinyl C1 to C4 alkanoate, with the preferred material being vinyl acetate.

10 The copolymer emulsion may include a C2 to C4 alkylene monomer, e.g. ethylene, typically in an amount from 5% to 40% by weight of total monomer. Another possible co-monomer is selected from the alkyl (C2 to C10) (meth)acrylate class e.g., butylacrylate or 2-ethyl hexylacrylate, which will preferably be present in an amount from about 10% to about 60% by weight of the total monomer.

15 Particularly preferred is a polymeric composition in which the polymeric composition comprises vinylacetate and alkylacrylate or a polymeric composition in which the alkylacrylate comprises butylacrylate. In another preferred embodiment of the polymeric composition the alkylacrylate comprises 2-ethylhexylacrylate.

20 A further class of functional co-monomer is carboxyl-containing monomers, e.g. acrylic acid, methacrylic acid, crotonic acid, itaconic acid etc. Hydroxyalkyl (meth)acrylate monomers, e.g. hydroxyethyl acrylate, may also be included. Typical levels are up to 5% by weight of total monomer. Other functional monomers e.g. sodium vinyl sulphonate and 25 acrylamide may also be included usually in small percentages. Preferred are compositions in which the weight ratio of vinylacetate : alkylacrylate: crosslinkable monomer is from 30 - 80 : 20 - 70 : 0.5 - 10, also preferred are polymeric compositions in which the weight ratio of vinylacetate : ethylene : crosslinkable monomer is from 60 - 90 : 10 - 40 : 0.5 - 10. Preferably the mixture of polymers consists substantially of vinylacetate, ethylene or alkyl(meth)acrylate ester and a crosslinkable monomer.

25 It is preferred to incorporate the sanitiser in one of the monomeric substances prior to polymerization, preferably in the vinyl ester.

To stabilise the latex one or more surfactants of the non-ionic or anionic type may also be included. Such surfactants are well known in the art and are described at length in: "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry & Birch, Interscience Publishers Inc. 1958. Protective colloids like e.g. polyvinyl alcohol may also be added.

30 Any suitable initiator can be used, in the case of thermal polymerization the use of ammonium- or alkali metal persulphate is convenient and in the case of redox initiation a persulphate, hydrogen peroxide or an organic peroxide is useful together with ascorbic acid or sodium metabisulphite as a reducing agent.

The copolymer emulsion can be prepared by using conventional techniques, which are well known in the art. Polymer synthesis (Vols I and II) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (Interscience 1968), provide more complete preparative details.

35 In a preferred embodiment of the invention the sanitiser is incorporated in a polymeric composition, which is prepared by emulsion- or suspension polymerization technique where the sanitiser is dissolved in monomeric material followed by polymerization under the influence of free radicals.

40 In another embodiment of the invention the sanitiser in a polymeric composition as material is in the form of an aqueous latex, which is obtained as the result of the polymerization reaction as such or after concentration thereof.

Another embodiment of the invention is the use of a sanitiser incorporated in a polymeric composition according to the present invention as a binding composition with incorporated sanitiser to bind and sanitise non-woven materials.

45 In another embodiment the invention provides non-woven material comprising a binding composition with incorporated sanitiser in which the amount of polymeric binder with incorporated sanitiser is from 10 to 45 % (w.w.) based on the weight of the fibres.

In another embodiment of the invention packaging material is provided which is coated with a polymeric binder with incorporated sanitiser according to the present invention.

50 Advantages of the non-woven materials according to the present invention is that they are less prone to biodeterioration and have a longer sanitary life due to slow release of the sanitiser, which even survives washing of the non-woven article and that the articles assist in good sanitary conditions in hospitals, laboratories and households.

The invention is illustrated by the following non-limiting examples. All parts, percentages and ratios are on a weight basis unless otherwise indicated.

Example 1

55 To a polymerisation reactor were charged 0.547 parts of nonylphenol ethoxylate 35 EO (Ethylen HA, tradename ex Akros U.K.), 0.418 parts sodium salt of n. dodecylbenzene-sulphonic acid (Arylan SC15, trademark ex Akros U.K.) (15% solution), 0.111 parts of sodium acetate and 61.0 parts of deionised water. The reactor was heated to 70°C and purged with nitrogen.

5 In a separate vessel, 1.172 parts of Ethylan HA, 3.216 parts of Arylan SC15, (15% solution), and 7.540 parts of a 45% aqueous solution of N-methylolacrylamide were dissolved in 31.984 parts of deionised water to form a second water phase. In a separate vessel, 2.070 parts of 2,2'-di-hydroxy-5,5'-dichloro-diphenylmethane (Panacide Technical Solid, ex Coalite U.K.) was dissolved in a monomer mixture comprising 34.735 parts of vinyl acetate and 42.382 parts of butyl acrylate. The solution of Panacide in monomers and the second water phase were mixed under agitation to produce a pre-emulsion.

10 When the reactor temperature was stable at 70°C, a mixture of 9.965 parts of vinyl acetate and 1.124 parts of butyl acrylate was charged, followed by a solution of 0.203 parts of ammonium persulphate in 1.608 parts of deionised water. The reactor contents were allowed to exotherm to 75°C, when the slow-addition of the pre-emulsion was commenced to last for 3½ hours. At the end of the pre-emulsion addition, a mixture of 3.766 parts of vinyl acetate and 4.635 parts of butyl acrylate was slow-added over 30 minutes. 30 minutes after the commencement of the pre-emulsion addition, a slow-addition of 0.111 parts of ammonium persulphate in 16.548 parts of deionised water was commenced to take 4 hours. The temperature was maintained at 75°C for the duration of the slow additions.

15 After the slow additions were complete, a solution of 0.055 parts of ammonium persulphate in 0.500 parts of deionised water was added, and the temperature was increased to 80°C for 1 hour. At the end of this period the temperature was reduced to 50°C, and solutions of 0.300 parts of ~~butyl hydroperoxide~~ in 1.000 part of deionised water, and 0.200 parts of sodium formaldehydesulphoxylate in 1.000 parts of deionised water were added over 30 minutes. A solution of 0.092 parts of an antifoaming agent (blend of mineral oil and silicon oil) in 1.000 parts of deionised water was added. The reactor was cooled and the product was discharged and filtered through nylon mesh to remove coagulum. The 20 resultant latex had a solids content of 47.14%, pH of 3.7 and viscosity of 0.61 Pa.s.

Comparative Example 1

25 To a polymerisation reactor was charged 0.536 parts of Ethylan HA, 0.409 parts of Arylan SC15, (15% solution), 0.109 parts of sodium acetate and 59.83 parts of deionised water. The reactor was heated to 70°C and purged with nitrogen.

30 In a separate vessel, 1.148 parts of Ethylan HA, 3.151 parts of Arylan SC15, (15% solution), and 7.388 parts of a 45% aqueous solution of N-methylolacrylamide were dissolved in 31.334 parts of deionised water to form a second water phase. In a separate vessel 38.734 parts of vinyl acetate and 47.078 parts of butyl acrylate were mixed. The monomer mixture and the second water phase were mixed under agitation to produce a pre-emulsion.

35 When the reactor temperature was stable at 70°C, a mixture of 9.763 parts of vinyl acetate and 1.101 parts of butyl acrylate was charged, followed by a solution of 0.199 parts of ammonium persulphate in 1.575 parts of deionised water. The reactor contents were allowed to exotherm to 75°C, when the slow-addition of the pre-emulsion was commenced to last for 4 hours. 30 minutes after the commencement of the pre-emulsion addition, a slow-addition of 0.109 parts of ammonium persulphate in 16.213 parts of deionised water was commenced to take 4 hours. The temperature was maintained at 75°C for the duration of the slow additions.

40 After the slow additions were complete, the temperature was increased to 80°C for 1 hour. At the end of this period the temperature was reduced to 50°C and a solution of 0.091 parts of an antifoaming agent (equal parts of mineral oil and silicon oil) in 1.630 parts of deionised water was added. The reactor was cooled and the product was discharged and filtered through nylon mesh to remove coagulum. The resultant latex had a solids content of 45.81%, pH of 4.25 and viscosity of 0.35 Pa.s.

Example 2

45 The binders of Example 1 and Comparative Example 1 were diluted with water to 20% solids, catalysed by the addition of 1% ammonium chloride w/w, and used to impregnate a light viscose web of weight 15 g/m², giving a pick-up of ca. 19.5%. The webs were dried and cured at 165°C on a rotary iron for 12 seconds. Strips of impregnated web of dimensions 200 x 50 mm were then tested for tensile strength on an Instron Tensiometer. The breaking load in kg and elongation at break in % was measured for dry samples, wet samples and samples dipped in solvent, (acetone).

	Example 1	Comparative Example 1
Dry Tensile Strength, kg	0.704	0.723
Elongation, %	26.03	23.94
Wet Tensile Strength, kg	0.265	0.254
Elongation, %	32.68	32.87
Solvent Tensile Strength, kg	0.118	0.145
Elongation, %	7.82	8.56

This shows that the Panacide does not adversely affect the performance as a non-woven binder.

Example 3

Non-woven fabrics were impregnated with binder formulations as detailed:-

	A	B	C
Latex of Example 1	260	-	-
Latex of Comparative Example 1	-	257.7	260
Wetting Agent*	2.1	2.1	2.1
Citric Acid	0.8	0.8	0.8
Water	337.1	327.9	337.1
Panacide Solid	-	2.3	-
Propylene Glycol	-	9.2	-

* = sodium salt of dioctyl sulphosuccinate (70% active)

Fabrics were cured, then some were washed cold at 30°C and some were washed hot at 70°C. Discs of each fabric were cut out and placed on to specific agar media. The media used were Nutrient Agar for bacteria and Rose Bengal, Chloramphenicol Agar and Malt Extract Agar for fungi and yeasts. The discs of fabric were then inoculated with an appropriate spore suspension inoculum, which contained ca. 10⁷ spores per ml. After incubation for 7 days at 30°C for bacteria and 27-28°C for fungi and yeasts the plates were examined and the amount of growth noted.

	No Wash	Cold Wash	Hot Wash
A	No Growth	No Growth	No Growth
B	Heavy Growth	Heavy Growth	Heavy Growth
C	Heavy Growth	Heavy Growth	Heavy Growth

This demonstrates that the inclusion of Panacide by encapsulation in a non-woven binder protects fabric impregnated with the binder, whereas fabric impregnated with binder which does not contain Panacide, or contains only post-added

Panacide does not protect the fabric impregnated with the binder. Similar results were obtainable with Triclosan and Chlorophene.

Claims

- 5 1. A sanitiser incorporated in a polymeric composition which polymeric composition comprises vinylester and alkyl(metha)acrylate and/or ethylene and at least one post polymerisation crosslinkable monomer.
- 10 2. A sanitiser incorporated in a polymeric composition as claimed in claim 1, in which the polymeric composition comprises vinylacetate and alkylacrylate.
- 15 3. A sanitiser incorporated in a polymeric composition as claimed in claim 1 or 2, in which the alkylacrylate comprises butylacrylate.
- 20 4. A sanitiser incorporated in a polymeric composition as claimed in claim 1 or 2, in which the alkylacrylate comprises 2-ethylhexylacrylate.
- 25 5. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 4, in which the crosslinkable monomer comprises N-methylolacrylamide and/ or an alkylester of N-methylolacrylamide.
- 30 6. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 5, in which the weight ratio of vinylacetate : alkylacrylate: crosslinkable monomer is from 30 - 80 : 20 - 70 : 0.5 - 10.
- 35 7. A sanitiser incorporated in a polymeric composition as claimed in claim 1, in which the weight ratio of vinylacetate : ethylene : crosslinkable monomer is from 60 - 90 : 10 - 40 : 0.5 - 10.
- 40 8. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 7, in which the sanitiser comprises a halogenated phenol derivative.
- 45 9. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 7, in which the sanitiser comprises 2,2'-dihydroxy-5,5'-dichloro-diphenylmethane.
- 50 10. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 9, in which the sanitiser(s) are present at a level of about 0.1 to 5% (w.w.) calculated on the amount of polymeric material.
11. A sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 10, in which the polymeric material is present in the form of an aqueous latex.
12. A process for preparing a sanitiser incorporated in a polymeric composition as claimed in any of the preceding claims, in which the material is prepared by emulsion- or suspension polymerization technique where the sanitiser is dissolved in monomeric material followed by polymerisation under the influence of free radicals.
13. Use of a sanitiser incorporated in a polymeric composition as claimed in any of the claims 1 to 11, characterized by using the material as a binder with incorporated sanitiser to bind and sanitise non-woven materials.
14. Non-woven materials comprising a polymeric binder with incorporated sanitiser according to any of the claims 1 to 11.
15. Non-woven material according to claim 14 in which the amount of polymeric binder with incorporated sanitiser is from 10 to 45 % (w.w.) based on the weight of the fibres.
16. Packaging material coated with a polymeric binder with incorporated sanitiser according to any of the claims 1-11.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 94 30 9133

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim							
A	EP-A-0 147 759 (GOODRICH CO B F) 10 July 1985 * page 1, line 26 - page 17, line 13 * ---	1,5,8, 11-14,16	D04H1/64						
A	EP-A-0 113 254 (TULTEX CORP) 11 July 1984 * page 1, line 20 - page 6, line 27 * ---	1,8,11							
A	EP-A-0 133 277 (AIR PROD & CHEM) 20 February 1985 * page 2, line 27 - page 11, line 36 * ---	1,5							
A	US-A-4 590 102 (ROSAMILIA PETER L ET AL) 20 May 1986 * column 2, line 41 - column 6, line 61 * -----	1,5							
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)						
			D04H						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>10 May 1995</td> <td>V Beurden-Hopkins, S</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	10 May 1995	V Beurden-Hopkins, S
Place of search	Date of completion of the search	Examiner							
THE HAGUE	10 May 1995	V Beurden-Hopkins, S							
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>									

